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MOLECULAR DYNAMICS OF NITRAMINES AND HIGH ENERGY
COMPOSITE MATERIALS

FINAL REPORT

Prepared for
Directorate of Aerospace Sciences
Air Force Office of Scientific Research
Bolling Air Force Base
District of Columbia 20332

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A study of the molecular dynamics of the solid phase of IMX and RDX was undertaken to learn the effects of thermal and pressure stress on these nitramines. Raman, nuclear quadrupole resonance, and nuclear magnetic resonance spectroscopy, mass spectrometry, X-ray methods and computer graphics were or are being employed. A complete analysis of the four polymorphs of IMX as a function of temperature and pressure by using Raman spectroscopy was made. A pressure-temperature phase diagram of the beta-to-delta-IMX solid phase transformation was developed. Computer graphics were employed to examine the inter- and intra-			


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molecular interactions that might play a role in thermal degradation of HMX. The positioning of atoms in the lattice is favorable for HONO, CH₂O and N₂O formation from the solid materials. Mass spectrometry is being used to examine in detail the possible differences in the product distribution during pyrolysis of the polymorphs of HMX. Nuclear resonance spectroscopy employing both the magnetic and quadrupole moments of nuclei in HMX molecule is being conducted to discover the specific molecular motions as HMX is heated from 77K through the beta-to-delta phase transformation. The results reveal a considerable increase in molecular motion in the lattice as it heats.

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I. Preamble

Much of the research described in this report has appeared or will shortly appear in our articles in the Journal of Physical Chemistry. So as not to repeat what is already widely available, this report will summarize the important conclusions of our studies and give the references to the journal articles where the work is presented in detail. We have ongoing projects which are in early stages at the moment. This work is briefly described here and will appear in later reports or journal articles as appropriate when it is completed.

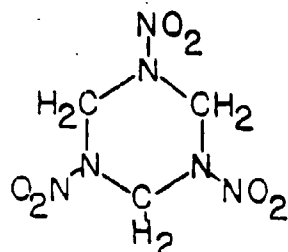
II. Background and Objectives

The thermal decomposition of materials is a field having broad theoretical scope and practical importance. Research related to thermal effects ranges from gas dynamics, combustion, flames and explosions on one end to the material science of heated materials on the other. Much current interest in the field of thermal decomposition of high energy materials stems from (1), interest in how energy is stored in materials, and (2), how the properties of materials undergoing thermal stress might be controlled.

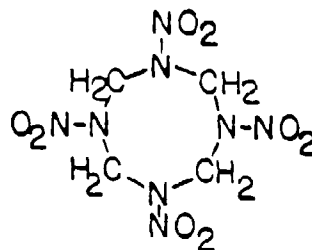
Research in this project has focused on the diagnosis of thermal processes in solids from a molecular point of view. The picture of thermal decomposition is clouded by the fact the system is a heterogeneous non-equilibrium one and is inherently "messy". Raman spectroscopy offers an opportunity to sort out some of the fundamental events in a way that cannot be realized by other spectroscopic techniques. Apart from the very desirable fact that the spectra give detailed molecular information, the Raman technique offers highly flexible sampling possibilities. Information can be obtained on a sample under conditions which approximate real use, rather than being idealized to suit the restrictions of the experimental method.

To this date our concern has been with the molecular and lattice dynamics that initiate thermal decomposition in ammonium perchlorate, HMX and RDX. Since Raman spectroscopy had not been used specifically to attack these kinds of problems prior to our attempts, we felt it wise to begin our studies in 1973 with the simplest ionic oxidizer, ammonium perchlorate (AP). AP is a high energy oxidizer whose gas phase and flame chemistry have been studied in some detail.¹ The nature of the solid phase during thermal decomposition was less well known. We were able to demonstrate that thermal decomposition of solid AP is triggered by the onset of essentially unhindered tumbling of the perchlorate ion in the solid phase.^{2,3} This fact became evident by the appearance of rotational wings on the E bending mode of the ion at the temperature where thermal decomposition is first detected. Apparently, the crystal lattice is destabilized by the rapid motion of the anion as a result of breakdown of the hydrogen bonding present. This mechanism for the initiation of thermal decomposition explains why K^+ -doped AP decomposes at a lower temperature than does pure AP.^{4,5} Raman analysis of the doped AP lattice confirms that K^+ lowers the temperature required to initiate ClO_4^- ion rotation. In addition, Raman spectral parameters were shown to be a useful in situ thermometer for measuring heat transmission into the crystal.³

Having developed the experimental methods needed to study thermal decomposition of oxidizers, we turned to organic molecules containing ring systems. Hexahydro-1,3,5-trinitro-s-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are monopropellants that store considerable energy. Their solid phase thermal properties are of great interest and were not well characterized from a molecular point of view at the time this work was begun.



RDX



HMX

Hence the research effort on this project has been directed toward the elucidation of the nature of the solid state of HMX and RDX under conditions of elevated temperature and pressure. The solid phase of a propellant plays an important role in the nature of the decomposition and burning of nitramine propellants. Thus investigation of solid state behavior under pressure-temperature stress is an important element in the overall modelling of HMX decomposition and combustion.

III. Approach:

Most of our research to date has employed Raman spectroscopy to diagnose molecular changes. Raman spectroscopy provides information on molecular vibrations in monopropellants under conditions which reasonably approximate those of real use. The information is controlled by molecular events and, as a result, is fundamental, detailed and highly descriptive of the processes that occur. We have also made use of X-ray methods, computer graphics, mass spectrometry, and nuclear quadrupole resonance spectroscopy in the course of the studies. Not all of the work proposed is complete and thus many of these studies are continuing under a new grant.

IV. Summary of Results:

The abstracts of the published work under this grant are given below and summarize the results.

- A. F. Coetz, T.B. Brill and J.R. Ferraro, Journal of Physical Chemistry, 82, 1912(1978).

Pressure Dependence of the Raman and Infrared Spectra of α -, β -, γ -, and δ -Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

Abstract

The Raman and infrared spectra are reported of the α -, β -, γ -, and δ -polymorphs of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) under pressure using a diamond anvil cell (DAC). The stability to pressure or the pressure-induced phase transitions were determined for each polymorph. Sample pressures up to 10 kbar were used in the Raman experiments; infrared spectra were recorded at pressures up to 54 kbar. The observed behavior of the polymorphic forms is as follows: β -HMX is stable up to 54 kbar and α -HMX is stable up to 42 kbar. γ -HMX converts to β -HMX at 5.5 kbar, and δ -HMX converts to a mixture of α - and β -HMX at pressures below 0.5 kbar. No new polymorphs were produced under pressure. An inverse relationship exists between temperature and pressure effects; the polymorph most stable at low temperature and having the smallest volume (β -HMX) is the most stable at high pressure. The infrared spectra (600 - 1700 cm^{-1}) of the solid HMX polymorphs at ambient pressure are reported for the first time without matrix effects. The -CH_2 - and -NO_2 vibrational regions ($>1200\text{ cm}^{-1}$) in the absence of the KBr matrix, and with the increased resolution obtained in the DAC, show minor differences from the KBr spectra reported in the literature.

- B. S.T. Sergio, U.S. NTIS Report, AD-A053155 (1978).

Studies of the Polymorphs of RDX

Abstract

Previous studies have using a hot-stage microscope indicate that two polymorphs of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) exist. The most stable form is α -RDX. A second form is a very unstable β -RDX form which rapidly converts to α -RDX. No further characterization of β -RDX has been published, but such a polymorph could be important in explosives technology. In an attempt to characterize the β -polymorph of RDX, a number of instrumental techniques were utilized. Laser Raman spectroscopy was used as an analytical probe since the change in ring conformation and/or crystal lattice packing, which one would expect to occur with a transition from the α - to β -polymorph,

would produce a change in the spectra. Analysis of spectral changes would provide qualitative information concerning the structure of the β -polymorph. Spectra of RDX in various matrices and up to the melting point were taken. An X-ray powder diffractometer was used in an attempt to verify the presence of β -RDX in a mixture of the two polymorphs when prepared from a thymol melt. Also, analysis of the powder patterns would provide information on the size and shape of the unit cell in a β -RDX crystal. Since the only analytical data available for the characterization of β -RDX are its optical crystallographic properties, a polarizing microscope was utilized to verify the presence of β -RDX prior to the initiation of selected experiments. No evidence of β -RDX was obtained in any experiment except the hot stage microscope.

C. F. Goetz and T.B. Brill, Journal of Physical Chemistry, 83, 340(1979).

Laser Raman Spectra of α -, β -, γ -, and δ -Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine and Their Temperature Dependence

Abstract

The laser Raman spectra of the four known polymorphs of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) have been recorded. Comparison of the spectra with the predictions of factor group analyses of α -, β -, and δ -HMX are presented. The spectra reveal that β -HMX contains a different ring conformation than do α -, γ -, and δ -HMX. α -, γ -, and δ -HMX have ring conformations which are similar to one another. γ -HMX appears to contain more anharmonicity in its vibrational motions and this may contribute to the fact that γ -HMX does not form thermally by solid-solid transformations from the other polymorphs, but readily converts to δ -HMX upon heating. The spectral regions which proved to be the most useful for identification of each polymorph are 300-550 and 700-1050 cm^{-1} . The lattice regions were not as useful because of the difficulty of recording some of the spectra near the exciting line. The solid-solid phase-transition behavior between the polymorph forms was studied at two heating rates and the Raman spectra recorded at isothermal conditions. The transitions observed were generally similar to those reported previously, but the transition temperatures differ somewhat. The gas-solid heat transfer methods used in these studies appears not to yield thermodynamic transition temperatures characteristic of equilibrium conditions.

- D. T.B. Brill and C.O. Reese, Journal of Physical Chemistry, 84, 1376(1980).

Analysis of Intra- and Intermolecular Interactions Relating to the Thermophysical Behavior of α -, β -, and δ -Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine.

Abstract

The relative stabilities of the β , α , and δ polymorphs of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine) were analyzed in terms of Coulombic forces. The internal contacts in the molecule show the feasibility of formation of HONO, CH₂O, and N₂O during pyrolysis. Intramolecular interactions cause the chair conformation adopted by β -HMX to be more stable than the chair-chair form of α - and δ -HMX. It was found that the total electrostatic energy of the heavy-atom intermolecular interactions in a shell of radius 3.75 Å around each atom follows the experimentally observed trend in polymorph stability at room temperature. Intermolecular interactions are dominated N...O and C...O attractions combined with O...O and N...O repulsions. Hydrogen bonding does not play an important role in determining the crystal structures adopted by HMX. The intermolecular forces are illustrated by use of computer graphics plots from ORTEP.

- E. A.G. Landers and T.B. Brill, Journal of Physical Chemistry, 84, 0000 (Dec. 25) (1980).

Pressure-Temperature Dependence of the β - δ Polymorph Interconversion in Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

Abstract

The sensitivity of the $\beta \rightleftharpoons \delta$ polymorph transition of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) to the combined effects of pressure and temperature has been determined in the solid phase using Raman spectroscopy. The N₂ gas pressure range was 0.1 - 138 MPa (0 - 2 x 10⁴ psig). In this pressure range the temperature for the $\beta \rightarrow \delta$ conversion increases from 176 to 210°C. The line representing the conversion appears to have a slope-break at 69 MPa (1 x 10⁴ psig). ΔH and ΔS for the conversion in the 0.1 - 69 MPa range are 10.1 kJ/mole and 2.34 J/°mole, respectively. In the 69 - 138 MPa range, ΔH is 17.7 kJ/mole and ΔS is 4.11 J/°mole. This transition is slightly dependent on the particle size for >63 μ HMX, but is significantly more sensitive to pressure and temperature in 3 μ HMX. The $\beta \rightarrow \delta$ and $\alpha \rightarrow \delta$ phase transition

temperatures were redetermined using slow heating and a new sample cell. By N_2 gas heating, the $\beta \rightarrow \delta$ transition occurred at $165^\circ C$ and the $\alpha \rightarrow \beta$ transition appeared at $193^\circ C$.

The above five projects are complete. We are currently involved in a number of studies which are not yet complete. A brief description of the purpose for carrying out these studies follows along with a summary of progress to date is presented here.

F. Pyrolysis Product Distributions of the HMX Polymorphs

The primary purpose of these experiments is to investigate the thermal decomposition of HMX in its polymorphic forms. The product distribution in the gas phase above solid HMX and solid HMX with additives is not well known. The electron impact, EI, mass spectra are relatively reproducible from one laboratory to another⁶ and small differences have been noted in the electron impact, EI, mass spectra of α - and β -HMX.⁷ However, the general mass spectrometric literature on thermally labile substances, our experience with mass spectra of thermally labile compounds,^{8,9} and preliminary experiments in this laboratory on the electron impact (EI) and chemical ionization (CI) mass spectra of HMX indicate that the mass spectra of HMX are strongly dependent on experimental parameters: source and probe temperatures, probe surfaces, sample heating rates, etc. The reported EI mass spectra of HMX contain essentially no molecular ions and it is not clear whether or not it is felt that undissociated HMX molecules are present to only a very small extent. CH_4 CI mass spectra of HMX have been reported which contain essentially no or reasonable amounts of MH^+ ions^{10,11} and the NH_3 CI mass spectra of HMX contains the $(M+NH_4)^+$ ion as the most abundant peak. Consequently one may infer that significant amounts of undissociated HMX molecules are present in the gas phase. The striking differences in the CH_4 CI spectra of HMX reported in references 10 and 11 may be due to both temperature differences and to

differences in the methods of sample introduction into the source of the mass spectrometer. We have observed that the CH_4 CI spectra of β -HMX are quite different when the samples are vaporized from a glass capillary in the well of a conventional direct insertion probe and when the samples are vaporized from the Teflon-coated tip of a probe that is within the ionization chamber.

The thermal decomposition, volatilization, and/or pyrolysis of HMX and certain HMX mixtures is being investigated mass spectrometrically. The studies involve linearly programmed and rapid ballistics heating of samples of the different polymorphs to establish the acceptable range of critical parameters necessary to obtain reproducible temperature/time profiles of ionic abundances, that is, to obtain time-resolved mass spectra. The majority of the work is being carried out with a Bendix Model 3012 Time-of-Flight mass spectrometer with continuous monitoring of five ions using a multichannel recorder and the initial studies will be made using low pressure electron ionization. Once the reproducibility of temperature or time profiles of characteristic ions has been established for one polymorph, comparisons will be made of the different polymorphs under as nearly identical conditions as possible to see if the decomposition/volatilization processes of the polymorphs are differentiable.

The effects of several experimental parameters on these thermal desorption spectra will be investigated: sample size, crystal size, crystal pretreatment, and gross crystal defects. In addition, probe heating rate, probe temperature, probe surface, and source temperature will be investigated for their effects on the reproducibility of ionic abundances and their temperature or time dependence. Possible wall effects on decomposition of HMX will be investigated by comparing the spectra obtained from samples in conventional glass capillaries with samples vaporized from a heatable probe

tip that may be placed within one mm of the ionizing beam of electrons. This probe will be similar in design to one made previously in this laboratory⁹ and will be made in our shops. A probe thermocouple and associated electronics will provide feedback to the temperature programmer as well as the multi-channel recorder. Preliminary experiments with a CEC 21-110B mass spectrometer and a similar probe indicate that a single crystal, ~175 μ m long, is sufficient to obtain spectra. We have access to a Phillips 501 Scanning Electron Microscope to examine the crystals in more detail. In addition to these experiments thermal decomposition or thermal desorption of HMX/LiClO₄ or HMX/TMETN solutions will be examined. Comparisons will be made of ionic distributions above the solutions and above the solid HMX at the same temperature.

Modification of the TOF mass spectrometer for chemical ionization studies will be made. Subsequently, experiments are planned to use the selectivity of chemical ionization to distinguish between ionic and neutral fragmentation processes. In addition to the experiments with the TOF mass spectrometer with its multiple-ion monitoring and fast scanning capabilities, high resolution mass spectra under EI or CI conditions will be obtained on other instruments for confirmation of elemental compositions.

The results on product distributions will be compared to our computer graphics studies (see D above) with the intent of providing a quantitative structure-reactivity picture of the HMX molecule in the chair-chair conformation as a function of lattice differences (compare α - and δ -HMX) and conformational differences (compare β - to α - and δ -HMX). Once and for all this should properly answer the question of the relationship of HMX pyrolysis products to the structure of the molecule.

Modifications have been made to the Bendix Model 3012 Time-of-Flight mass spectrometer involving a 90 degree rotation of the source and drift tube liner. This progress to date will allow an additional diffusion pump to be fitted to the source housing via flanges in our possession. In addition a plexiglass plate has been mounted on the source housing to allow visual inspection of the source. The resolution and sensitivity of the instrument has not changed with respect to previous performance. A dual gas manifold has been built and interfaced to the T.O.F. source with a gold foil leak. Plans for probes and a probe vacuum lock are drawn. Construction is expected to begin in the near future.

Thermal desorption experiments on β -HMX have been carried out with a CEC (duPont) 21-110 B mass spectrometer. A number of ion intensity vs. temperature profiles were reconstructed from computer-acquired scanned mass spectra. These data, however, were not reproducible. The irreproducibility resulted from the difficulty of reproducing very small sample sizes, instabilities in the computer interface and a cold spot in the outlet of the heatable direct insertion probe, which led to sample condensation and subsequent slow vaporization. Rapid heating ($\sim 75^\circ\text{C}/\text{sec}$) experiments were carried out with a heatable in-beam probe. This probe permits easy handling of small samples and eliminates in-probe condensation problems. The intensities of two ions were monitored by rapid switching of accelerating and electric sector voltages. Data were obtained by an oscillographic recorder. These experiments were relatively reproducible and indicate the advantage of using an in-beam probe.

Thermogravimetric analysis experiments on β -HMX were performed at a variety of heating rates. The thermograms obtained indicate a change in reaction mechanism with heating rate. Areas of controlled and uncontrolled thermal degradation are indicated. No significant contamination of samples

for recrystallization solvent or other impurities was observed. Although the T.G.A. experiments were not carried out under vacuum conditions, it is expected that the data will roughly parallel data obtained by a thermal desorption mass spectrometry experiment. Differential thermal analysis experiments confirmed the expected beta-to-delta-HMX phase transition and ruled out the possibility of extensive RDX contamination.

The use of a programmable hot stage polarizing microscope allowed visual observation of the change in crystal structure with temperature. After heating to approximately 250°C and cooled crystalline clusters which correspond with published photographs of delta-HMX were noted. A glass stage cover provided a cool surface on which very small needle like crystals formed. They are presumed to be alpha HMX.

At present multiple-single ion monitoring experiments are being carried out under electron impact and chemical ionization conditions with a newly acquired duPont 492-B mass spectrometer.

This research project has only been underway for about two months and consequently no final conclusions can be expected until well into 1981-82.

G. Molecular Motions in HMX

Molecular motions control many of the properties of solids. The study of the lattice dynamics of HMX yields information on how the solid state controls the thermal properties of the monopropellant.

Vibrational spectroscopy (Raman and infrared) has been used successfully to characterize the α -, β -, γ -, and δ -polymorphs of HMX as a function of temperature and pressure. The Raman proved to be ideal for these diagnostics. However, leakage of vibrational energy among the bending and stretching modes as a function of temperature and pressure made it difficult to

specify the details of the process. Nevertheless, motions are still important. Their elucidation requires a somewhat different approach. The important motions of HMX at room temperature and those leading to the phase transition may have their origin in the lower temperature domain. As the temperature is increased, changes in the lattice occur due to the onset of motion. More drastic changes occur when β -HMX becomes δ -HMX at approximately 163°C.

A sensitive tool was sought to probe these changes in molecular motion over a broad temperature range (77°K to 475°K). Nitrogen-14 nuclear quadrupole resonance spectroscopy (^{14}N NQR) and nuclear magnetic resonance spectroscopy (NMR) are sensitive techniques for determining molecular motions since they sample information in the time frame of the motions. ^{14}N NQR is more sensitive to slow molecular motions than is NMR. For this reason NQR spectroscopy was chosen as the primary tool for the study of the molecular motions in HMX.

In NQR spectroscopy the coupling between a quadrupolar nucleus and an inherent electric field gradient (EFG) generated by neighboring electrons is measured.¹² This coupling is measured by the quantized absorption of radiofrequency (rf) energy by the quadrupolar nucleus. In addition, the rate at which the nucleus relaxes back to its original state after absorbing the rf energy is a sensitive measure of the motion present.

^{14}N NQR frequencies, linewidth and spin-lattice relaxation times as a function of temperature from 47 to 475°K are being studied by using transient techniques. Studies have appeared of this type on other molecules. For example, Tzalmona and Kaplan¹³ studied quadrupole frequency and spin-lattice relaxation times (T_1) of N,N'-dimethylpiperazine from 77°K up to the melting point (~276°K) by using pulsed ^{14}N NQR. Using the T_1 data they found that rotation of the CH_3 group occurs in the range of 120-200°K and hindered rotation of the entire molecule exists above 200°K. Recently, a study of

s-triazine using ^{14}N NQR to measure quadrupolar frequencies, linewidths and spin-lattice relaxation times as a function of temperature (77 to 280°K) was reported.¹⁴ The second-order phase transition (hexagonal to monoclinic) at 199°K was studied in detail using frequency and relaxation measurements. The dependence of linewidth and T_1 measurements on temperature was used to determine that the s-triazine molecule undergoes rotation about its three-fold axis at temperatures above 210°K.

To date the ^{14}N NQR frequencies for the ring nitrogens in 6-HMX have been measured between room temperature and 143°C (298 to 415°K). The data show that there are two different types of nitrogen nuclei in the ring, as expected from symmetry requirements. Figure 1 shows the coupling constants (e^2qQ/h) of the two nitrogen sites (N-I and N-II), calculated from the frequency measurements. The data show the typical decrease in e^2qQ/h as the temperature increases. This decrease is due to a decrease in the EFG by the increased vibrational motions of the molecule.¹⁵ The curvature found in Figure 1 should increase as the temperature approaches the phase transition. A discontinuity will mark the phase transition.

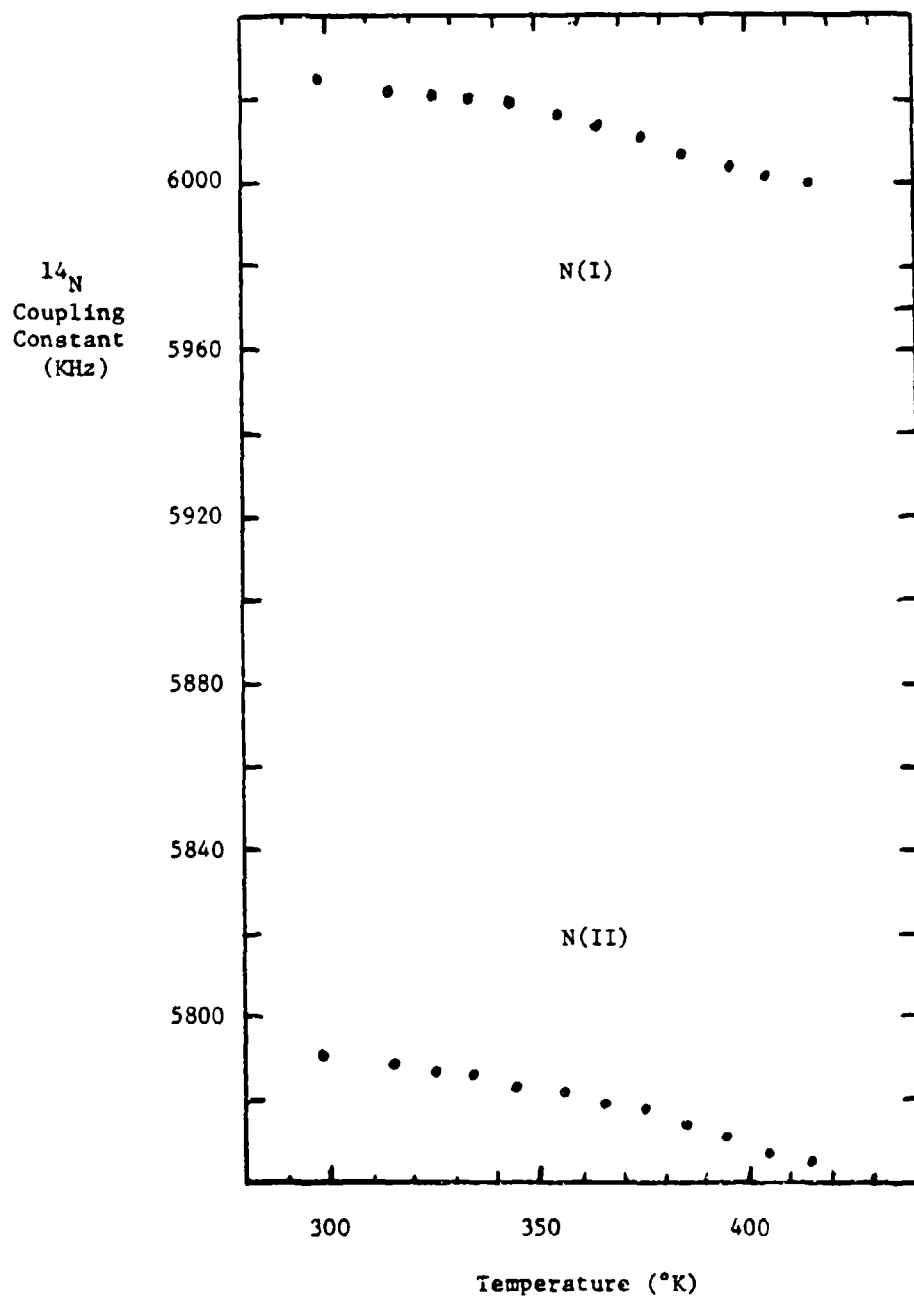
Spin-lattice relaxation times to date have only been measured for a few temperatures. These data are presented in Table 1. Two preliminary remarks can be made about the data. The first pertains to the large change in the values of T_1 on going from 77°K to 298°K. This change shows that the lattice is not rigid at room temperature. Appreciable motion exists. The second pertains to the difference in the T_1 values for the different nitrogen sites. This difference may result from directional motion in that one side of the HMX molecule may have more fluxional character than the other.

The ^{14}N NQR data so far collected are far from complete. Much more data will be collected before any specific conclusions are made about the specific motions in HMX. However, the preliminary results obtained appear very

Table 1. Spin-lattice relaxation times for ^{14}N in HMX at selected temperatures

<u>Temperature, °C</u>	<u>T₁ (seconds)</u>	
	<u>N(I)</u>	<u>N(II)</u>
40	1.57	1.78
36	1.21	2.0
25	2.53	2.68
10	1.90	1.57
-92	4.73	3.16
-196	16.25	16.03

Figure 1. A plot of the coupling constants of the two ring nitrogen sites as a function of temperature.



promising for providing a detailed model of the molecular dynamics of HMX as it heats toward the rapid decomposition stage.

V. Conclusions

1) Laser Raman spectroscopy was shown to be a useful and sensitive method for distinguishing and studying polymorph interconversions under conditions of elevated temperature and pressure.

2) A pressure-temperature phase diagram of HMX was developed from atmospheric up to 20,000 psi. A slope-break in the $\beta \rightarrow \delta$ HMX solid phase transition was observed. The events that cause slope-breaks in the dP/dT data for the solid-solid transitions may play a role in propellant combustion instability and perhaps even DDT phenomena. If molecular effects occur to create new phases, then these phases can produce different combustion rates, products, stabilities and fracturing. There does exist a slope-break in the $\beta \rightarrow \delta$ interconversion at 10,000 psi which was not known previously.

3) The thermodynamic parameters for solid-solid phase transitions can be determined in pressure domains studied. It might be tempting to extrapolate the data beyond 20,000 psi. However, noting the break at 10,000 psi, dP/dT may increase, decrease or remain the same above 20,000 psi. This leads to the provocative questions of what the nature of solid HMX is under pressures of gun barrels and explosions.

4) The $\beta \rightarrow \delta$ transition temperature is more sensitive to pressure than temperature. Since rocket motor temperatures are much greater than those employed in this study and pressures are in the 3000-7000 psi range, it is safe to conclude that the δ -polymorph is the stable form of HMX in rocket motor conditions. Only a small area of the surface of the HMX crystallites rather than the entire crystal needs to be converted to the δ -form and function as the active species in the decomposition of HMX.

5) The pressure-temperature conditions for the $\beta \rightarrow \delta$ conversion is slightly dependent on the size of the particles employed in the experiment. β -HMX is more stable in large crystals while δ -HMX is favored in the small crystals.

6) Computer graphics studies of the HMX polymorphs show the feasibility of HONO, N_2O , and CH_2O formation in HMX by intramolecular mechanisms.

7) Relaxation data on the ^{14}N ring nuclei look very promising for elucidating the types of motions that exist in HMX as it heats. β -HMX appears not to be a rigid lattice above room temperature.

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VI. Professional Personnel

1. Frank Goetz

Frank joined the project in the Fall of 1974 when he came to graduate school at the University of Delaware. In 1978 he was awarded a Ph.D. for his dissertation entitled "Molecular Dynamics of Selected Solid Propellants." Dr. Goetz spent 1978-80 at AFRPL as a Research Physical Scientist working on combustion bomb studies with Dr. Dave Mann. In late 1980, he assumed a position with Thiokol Corporation, Elkton, MD.

2. Captain Stephen T. Sergio

Captain Sergio (U.S. Army) came to Delaware in the Fall of 1976 to work toward an M.S. degree. He was awarded an M.S. in 1978 for his thesis entitled "Studies of the Polymorphs of HMX." Captain Sergio continues to serve in the U.S. Army.

3. Albert G. Landers

Al Landers came to Delaware in the Fall of 1976 to begin studies toward an M.S. degree. After completing his M.S. in another area, he joined the project in 1978. Al expects to complete his Ph.D. research in mid-1981. His dissertation will be titled "Thermophysical Properties of Nitramines."

4. Russell C. Spreen

Russ is working on mass spectrometry on nitramines for his Ph.D. degree. He worked quarter-time in 1979-80 and is full-time 1980-81 in this project. He came to graduate school in 1977 and is working under the direction of Dr. M. S. B. Munson and me.

5. Undergraduates

Two undergraduates, Clifford O. Reese and Cheryl Ward, have worked on the project for their senior research. Cliff is currently employed by Air Products and Cheryl works for Hercules in their explosives branch.